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(54) Process for cleaning copper base materials and regenerating the cleaning solution.

(57) Copper and copper base alloy are cleaned or etched using 1N to 5N aqueous peroxydisulfuric acid as the etching or cleaning solution. Spent solution is electrolytically regenerated by feeding the spent solution as an anolyte to a compartmental electrolytic cell using 10-50% aqueous acid as the catholyte and applying an electric current across the cell.

EP 0 138 531 A1

ACTORUM AG

PROCESS FOR CLEANING COPPER BASE MATERIALS
AND REGENERATING THE CLEANING SOLUTION

This invention relates to a process for cleaning copper base alloys using an aqueous peroxydisulfuric acid solution and for regenerating the spent cleaning solution.

The fundamental cleaning medium used in the copper industry is sulfuric acid at a strength of about 10 to 15% by volume. The extensive use of sulfuric acid is based on the fact that for most brasses and high copper alloys, the annealing oxides are readily soluble in mineral acids. This produces very rapid oxide removal and the resulting cleaning process is, therefore, readily amenable to a short immersion time, continuous operation.

However, an increasing number of copper alloys now contain elements which form insoluble, refractory-type oxides. For these alloys, alternative cleaning procedures have been developed. These alternative cleaning procedures generally involve adding an oxidant such as sodium dichromate or hydrogen peroxide to the cleaning solution. While sodium dichromate has been used effectively for years, its use has been discontinued because of its known high toxicity and restrictions on waste treatment and discharge level. While hydrogen peroxide does not suffer from these disadvantages, it is limited by its inherent stability problems. Hydrogen peroxide will decompose to water plus oxygen during storage. In addition and more importantly, the decomposition

of peroxide is greatly accelerated by elevated
temperatures and/or the presence of dissolved copper
in the cleaning solution. These factors limit the
maximum etching rates that can be obtained with
5   solutions containing hydrogen peroxide.

     In response to these shortcomings and the need
for an effective oxidizing cleaning solution,
attention has turned to persulfate solutions. The
use of persulfate is attractive for a copper cleaning
10   operation because the end products of the reaction of
persulfate with copper are sulfuric acid and copper
sulfate. As such, no special waste water treatment
is required. Furthermore, the depleted or spent
persulfate solution may be regenerated and the copper
15   in the depleted solution reclaimed. Typically, the
persulfate cleaning solutions comprise an aqueous
solution containing a persulfate salt such as ammonium
persulfate or sodium persulfate. Persulfate salts
have been used because they are readily
20   available. U.S. Patent Nos. 2,978,301 to Margulies
et al., 3,475,242 to Radimer, 3,671,344 to Chiang
et al., 3,887,405 to Fong et al. and 4,144,144 to
Radimer et al. illustrate the use of aqueous
persulfate salt solutions to etch copper materials.

25   The use of electrochemical cells to regenerate
spent solutions and to reclaim metal values from
the spent solutions are well known in the art.
Typically, these cells have at least one anode chamber
and at least one cathode chamber physically separated
30   by a membrane. Depending upon the type of solution
being regenerated and the chemical reactions sought
to be produced, the membrane generally comprises
either an ion exchange member or a microporous
separator. The spent solution is used as either
35   the anolyte or the catholyte. U.S. Patent

Nos. 2,748,071 to Eisler, 2,865,823 to Harris et al.,
3,761,369 to Tirrell, 3,764,503 to Lancy et al.,
4,051,001 to Inoue et al., and 4,149,946 to Burke
illustrate some of the electrochemical cells to

5 regenerate the spent cleaning solutions.

It has been suggested in the prior art to
regenerate persulfate etchants using electrochemical
cells. In one such persulfate etchant regeneration
technique, the spent etchant is treated to remove a

10 substantially persulfate-free mixture containing
ammonium persulfate and the corresponding metal
sulfate. The substantially persulfate-free mixture
is then transferred to the cathode chamber of an
electrochemical cell where it is used as the

15 catholyte. The remainder of the spent solution is
transferred to the anode chamber of the cell where
it is used as the anolyte. The cathode and anode
chambers of the cell are separated by a diaphragm
which permits at least hydrogen ions to pass freely

20 between the anolyte and the catholyte while preventing
any substantial amounts of persulfate in the anolyte
from mixing with the catholyte. By passing an
electric current between the anolyte and catholyte,
metal is plated out of the cathode and persulfate

25 values are produced at the anode. U.S. Patent
No. 3,406,108 to Radimer et al. illustrates this
technique for regenerating spent persulfate etchants.
The primary deficiency of this technique is its
complexity which renders it commercially unacceptable.

30   A second and simpler technique is illustrated in
U.S. Patent No. 3,470,044 to Radimer. In this
technique, the spent aqueous ammonium persulfate
etching solution is used as the anolyte or an
electrochemical cell. An electrolyte such as an

35 acidic bisulfate or a bisulfate containing electrolyte

is used as the catholyte of the cell. The cathode
and anode sections of the cell are separated by a
cathodic exchange membrane which permits the
dissolved metal ions to pass from the anolyte into

5   the catholyte but which prevents any substantial
amount of persulfate in the anolyte from mixing
with the catholyte. By passing an electric current
through the catholyte and the anolyte, dissolved
metal is removed from the solution at the cathode

10 and sulfate values are converted to persulfate values
at the anode.

While simpler, this second technique is believed
to be inefficient and commercially unacceptable. The
production of temperature sensitive, oxidizing

15 cleaning solutions such as persulfate etchants often
require electrolyte temperatures to be maintained
within certain critical limits during processing.
Therefore, an electrochemical cell for regenerating
such a temperature sensitive solution should have

20 some means for controlling electrolyte temperature.
Furthermore, special anodes are often required to
improve cell efficiency. Such temperature control
means and special anodes are known in the art.
U.S.S.R. Patent Nos. 311,502 and 470,307 both to

25 Markov et al. illustrate some special anode
constructions.

In accordance with the present invention, a
relatively simple but yet highly efficient process
for cleaning copper base materials is provided. The
copper base material is cleaned by immersion in an
5   aqueous peroxydisulfuric acid solution containing
peroxydisulfuric acid in a concentration in the range
of about 1N. to about 5N., preferably from about 1.5N.
to about 2.5N. The cleaning of the copper base
material is carried out with the solution having a
10 temperature in the range of about 15°C to about 30°C,
preferably from about 20°C to about 25°C.

As the amount of copper dissolved in the cleaning
solution increases and/or the amount of peroxydisulfuric
acid becomes substantially depleted, the etching rate or
15 cleaning power of the solution decreases. When the
cleaning power or etching rate of the solution reaches
a level where it is no longer feasible to clean the
copper base material within commercial time
constraints, the solution is withdrawn from the cell
20 and replaced by a fresh cleaning solution.
Thereafter, the withdrawn spent cleaning solution is
recirculated to an electrolytic cell for regeneration.

In accordance with the present invention, the
spent cleaning solution is introduced into the anode
25 chamber of the electrolytic cell for use as an
anolyte. An aqueous sulfuric acid solution containing
from about 10% to about 50%, preferably about 15% to
about 25%, by volume sulfuric acid is introduced into
each cathode chamber of the cell as a catholyte. The
30 anode chamber is preferably separated from each

cathode chamber by a membrane-type structure. By
applying an electric current across the cell, copper
from the spent or depleted cleaning solution is plated
out at the cathode and sulfate ions are oxidized to
5 persulfate ions at the anode.

It has been found that overall efficiency of the
cell can be increased by making a halide addition to
the anolyte. Depending upon the halide used, the
addition would be in the range of about 10 ppm to
10 about 500 ppm. For example, the halide addition may
be either from about 100 ppm to about 200 ppm of a
chloride such as hydrochloric acid or from about
50 ppm to about 100 ppm of a fluoride such as
hydrofluoric acid. As well as increasing cell
15 efficiency, the halide addition has been found to
decrease the rate of decomposition of the regenerated
persulfate acid solution without significantly
decreasing its cleaning power.

The apparatus described herein in connection with
20 the accompanying drawings provides a means for
practicing the process of the present invention.

Figure 1 is a schematic representation of a system for
cleaning metal strip and regenerating the cleaning solution.

Figure 2 is a cross-sectional view in partial
25 cross section of an electrochemical cell for
regenerating the spent cleaning solution.

Figure 3 is a graph illustrating the etching rate of
peroxydisulfuric acid as a function of its composition.

Figure 4 is a graph illustrating the stability
30 of peroxydisulfuric acid as a function of time and
temperature.

Figure 5 is a graph illustrating the stability
of peroxydisulfuric acid with a halide addition as a
function of time.

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Figure 6 is a graph illustrating the effect of temperature on cell efficiency and peroxydisulfuric acid generation.

Figure 7 is a graph illustrating the effect of current density of generation of peroxydisulfuric acid using the cell of Figure 2.

The present invention is concerned with effectively cleaning or etching copper base materials including copper and copper alloys. The copper base materials to be cleaned may have any form. For example, the materials may be in strip form, tube form, rod form, wire form or shaped into an article. Furthermore, the cleaning may be carried out either batchwise or continuously. For the purpose of illustrating the present invention, reference will be made to cleaning copper or copper alloy strip in a continuous fashion.

Referring now to Figure 1, a system for cleaning the copper or copper alloy strip is illustrated. Since it is no longer economically justifiable to immediately discard and replace spent cleaning solutions, the cleaning system of Figure 1 includes an electrochemical cell 14 for regenerating the depleted cleaning solution. The copper or copper alloy strip not shown to be cleaned is passed through the cleaning tank 10 containing a cleaning solution in accordance with the present invention. The strip may be passed through the tank 10 in any suitable manner known in the art. If necessary, the strip to be cleaned may be subjected to a mechanical cleaning action such as abrasion or another pretreatment, e.g. being passed through a boiling caustic solution prior to entering the tank 10. The type of pretreatment used will of course depend upon the material being cleaned and the nature of the contaminants being removed.

    In accordance with the present invention, the
cleaning solution in the tank 10 comprises an aqueous
peroxydisulfuric acid solution containing
peroxydisulfuric acid in a concentration of from
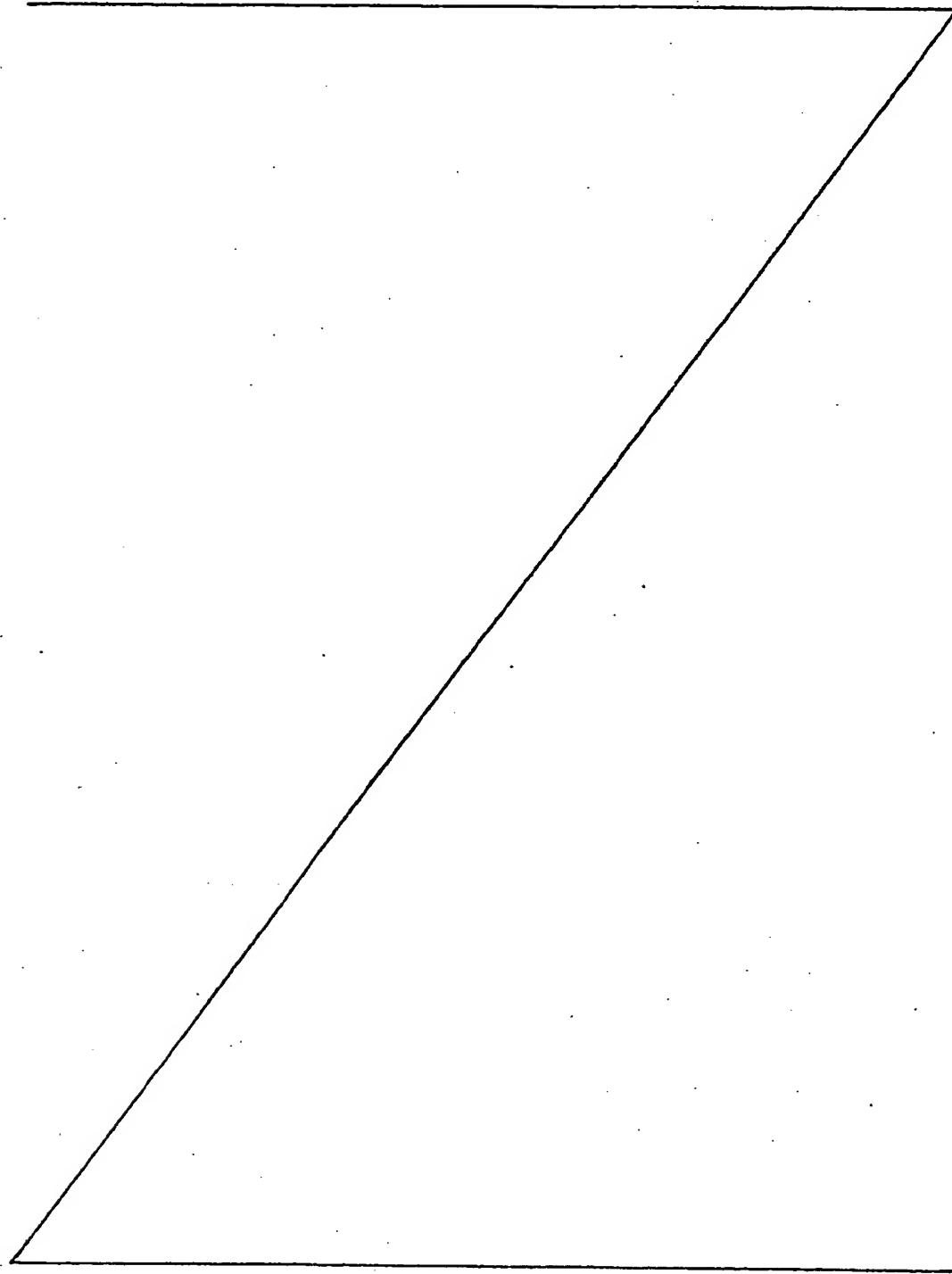
about 1N. to about 5N. Peroxydisulfuric acid in
such concentrations has been found to be an effective
cleaning agent. While similar cleaning effectiveness
has been obtained using persulfate salt cleaning
5   solutions such as aqueous sodium persulfate or
ammonium persulfate solutions, it is preferred in
accordance with this invention to use a peroxy-
acid solution rather than a persulfate salt solution
for the following reasons. The presence of additional
10 ions such as Na^+ or NH_4^+ ions in a persulfate salt
solution can lead to the production of undesirable
products, e.g. ammonia. Furthermore, they complicate
the regeneration process since the additional ions,
i.e. Na^+ or NH_4^+ as well as the useful persulfate ions
15 have to be replenished. In a preferred embodiment of
the cleaning solution of the present invention,
peroxydisulfuric acid is present in a concentration of
about 1.5N. to about 2.5N.

Since peroxydisulfuric acid tends to decompose
20 more rapidly at elevated temperatures, it has been
found to be particularly advantageous to carry out
cleaning at a solution temperature in the range of
about 15°C to about 30°C, preferably from about 20°C
to about 25°C. If needed, the tank 10 may be provided
25 with a suitable cooling system not shown to remove heat
and maintain the cleaning solution within the desired
temperature ranges.

An aqueous peroxydisulfuric acid solution tends to
decompose sequentially as follows:

30 $$H_2S_2O_8 + H_2O \rightarrow H_2SO_5 + H_2SO_4 \qquad (1)$$
$$H_2SO_5 + H_2O \rightarrow H_2O_2 + H_2SO_4 \qquad (2)$$
$$2H_2O_2 \rightarrow 2H_2O + O_2 \qquad (3)$$
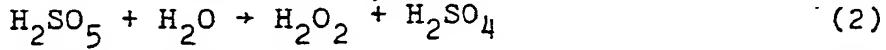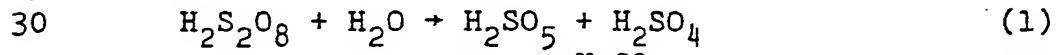
It has been surprisingly found that as the peroxydisulfuric acid
$H_2S_2O_8$ decomposes to a combination of peroxydisulfuric acid
35 $H_2S_2O_8$ + peroxymonosulfuric acid H_2SO_5 that the etching rate of
the cleaning solution tends to increase. Thereafter, the etching

rate remains substantially constant until $H_2S_2O_8$ changes almost completely.

As the copper or copper alloy strip passes through the cleaning solution, copper ions will dissolve into the solution and the following reactions typically take place:

$$H_2S_2O_8 + Cu \rightarrow Cu^{2+} + H_2SO_4 + SO_4^= \qquad (4)$$
$$H_2SO_5 + Cu \rightarrow CuSO_4 + H_2O \qquad (5)$$
$$H_2O_2 + H_2SO_4 + Cu \rightarrow CuSO_4 + 2H_2O \qquad (6)$$
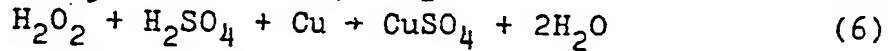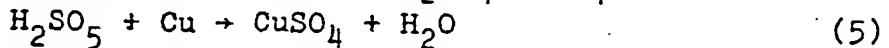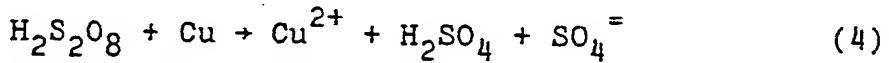
As a result, the depleted cleaning solution tends to contain some $H_2S_2O_8$, H_2SO_5, H_2O_2, H_2SO_4 and Cu^{2+}.

If too much copper is present in the depleted solution, $CuSO_4$ crystals could form. To prevent this from happening, it is desirable to withdraw the depleted solution before any significant copper ion level is reached. To this end, the tank 10 may be provided with means not shown for monitoring the bath condition. The monitoring means may comprise any suitable detection means known in the art to monitor any desired parameter such as bath temperature and/or copper concentration.

The cleaning tank 10 may also be provided with means not shown for agitating the cleaning solution to insure that fresh cleaning species contact the copper or copper alloy strip at all times. The agitating means may comprise any suitable stirring device known in the art such as one or more impellers not shown driven by a power source not shown.

After the cleaning power of the solution has been depleted so that cleaning cannot be carried out within a commercially acceptable time, the spent peroxydisulfuric acid solution is withdrawn from the tank 10 to the regeneration cell 14 via flow line 16 and valve 18. In a preferred embodiment of the present invention,

the spent solution is introduced into the cell 14 as
an anolyte.

Referring now to Figure 2, the regeneration cell
14 preferably has a central anode chamber 12 containing
5   an anode 48 and a pair of cathode chambers 20, each
containing a cathode 50. A physical separator 22
separates the anode chamber 12 from each cathode
chamber 20. The physical separators 22 are primarily
used to substantially prevent mixing of the products
10   in the anode and cathode chambers and may be mounted
in the cell 14 in any suitable manner. The physical
separators 22 may either be a diaphragm such as a
microporous polyethylene diaphragm or an ion exchange
membrane such as a cation exchange membrane, e.g. a
15   Nafion membrane. A diaphragm would be used where it
is desired to have a restricted bulk flow from one
chamber to another without any preference to the
charge of the ions passing therethrough. An ion
exchange membrane would be used where it is desired to
20 . substantially prevent any bulk flow while permitting
only the flow of certain preferred ions across the
membrane.

The anode 48 is the most complex structure in the
cell 14 because of the variety of roles that it plays
25   during cell operation. At a bare minimum, the anode
48 comprises at least one hollow tube 34 or conduit
through which, for reasons to be explained hereinafter,
a heat exchange medium flows, at least one current
collector 52 bonded to each tube 34 and at least one
30   electrochemically active portion 54 bonded to each
tube 34. In a preferred construction, the anode 48
comprises a grid-like structure formed by a plurality
of spaced-apart substantially parallel tubes 34, a
plurality of spaced-apart substantially parallel
35   current collectors 52 arranged substantially

transverse to the tubes 34, and a plurality of
electrochemically active portions 54 located on each
tube 34 substantially adjacent to and between the
location where each current collector 52 is bonded to
5   each tube 34.

Each of the tubes 34 is formed from an
electrically conductive material 34. While any
suitable electrically conductive material may be used,
it has been found to be desirable to form the tubes 34
10 from titanium or a titanium alloy.

The current collectors 52 preferably each comprise
a pair of spaced-apart strips of electrically
conductive material. Each strip may be contoured to
form good electrical contact with each tube 34. The
15 strips may be bonded to the tubes 34 in any suitable
manner known in the art, e.g. spot welding. To promote
a substantially uniform current distribution throughout
the cell, the current collectors 52 are substantially
uniformly distributed over the length of each tube 34.
20 The number, the spacing and the size of the current
collectors 52 depend upon the range of current
densities used in the cell and the operating electrode
surface area. While any suitable metal or metal alloy
having good electrical conductivity properties may be
25 used to form the current collectors 52, titanium or one
of its alloys is a preferred material.

The electrochemically active portions 54 are
preferably formed by metal members bonded to the tubes
34. For example, a plurality of metal rings can be
30 spot welded to or inlayed in the tubes 34. The extent
of the portions 54 and their surface area depend upon
the range of current densities used during cell
operation. If needed, the portions 54 could cover the
total electrically conductive area exposed to the
35 anolyte. While the portions 54 may be formed from any

suitable metal or metal alloy, it is preferred to form them from platinum or one of its alloys because platinum forms oxides which slow down oxygen evolution at the anode 48. In a most preferred construction,
5 the portions 54 are formed from bright recrystallized platinum.

The cathode 50 in each cathode chamber 20 may be formed from a metallic mesh type structure such as a brass screen. It is desirable that the mesh structure
10 have at least about 50% of its surface area open to promote good mass transport from the surrounding catholyte and better usage of the physical separators 22. Preferably, each cathode has about 50% to about 70% of its surface area open.

15 The removal of copper deposited on the cathode may be done in either a batchwise or a continuous manner. If done in a batchwise manner, the entire cathode structure may be removed and replaced. If done continuously, the cathode 50 may be formed from
20 an endless metallic mesh belt not shown rotated by a suitable drive motor not shown. A metal removing device not shown such as a conventional scraping knife or blade may be used to remove the plated metal from the belt.

25 The anode 48 and the cathodes 50 may be electrically connected to any conventional power supply not shown known in the art. Preferably, the anode 48 is connected to the current source or power supply via one or more copper busses not shown
30 attached to the current collectors 52.

35

The process of the present invention replenishes the persulfate values in the spent solution by electrochemically oxidizing sulfate ions to persulfate ions. To accomplish this, an aqueous sulfuric acid

5 solution is introduced into the cell 14 as the catholyte. The aqueous sulfuric acid solution may be supplied to and circulated through each cathode chamber 20 by a circulation loop 24. The circulation loop 24 may have a pump 26 to circulate the catholyte

10 as desired. Circulating the catholyte is desirable to help the efficiency of the system, particularly its cooling efficiency. In a preferred manner of using the cell 14, the catholyte flows through the chambers 20 in the same direction that the anolyte flows through

15 the anode chamber 12.

It has been found that to generate the needed concentration of peroxydisulfuric acid for the cleaning solution, the catholyte should contain from about 10% to about 50% by volume sulfuric acid. Preferably, the

20 aqueous sulfuric acid solution catholyte contains from about 15% to about 25% by volume sulfuric acid. It has been found that such concentrations assist in reducing the activity of water and, therefore, the evolution of oxygen at the anode.

25 Since the persulfate ion is relatively unstable in solution and its concentration tends to decay rapidly in time, it is desirable to maintain the catholyte and anolyte within a temperature range of about 0°C to about 20°C during the regeneration process. Preferably,

30 the catholyte and anolyte are maintained at a temperature in the range of about 0°C to about 10°C. Control of heat build-up in the anolyte also helps to favor the production of persulate values as opposed to the production of peroxide values.

35

To maintain the temperature of the anolyte and
the catholyte within the desired limits, a heat
exchange medium is circulated through the anode
chamber 12. The heat exchange medium may comprise any
5   suitable heat exchange fluid known in the art such as a
refrigerated aqueous glycol solution. The heat
exchange fluid may be circulated through the chamber
12 by heat exchange loop 28. Heat exchange loop 28
generally comprises a pump 30 for circulating the heat
10   exchange fluid, a unit 32 for cooling and/or heating
the heat exchange fluid, and the hollow tube or
tubes 34 forming part of the anode 48 in the chamber 12.
The heat exchange fluid preferably flows through the
heat exchange loop 28 so that the fluid in each tube
15   34 travels in a direction counter to the flow direction
of the electrolyte in the chamber 12.

          To further assist in maintaining cell temperature
within the desired limits, the circulation loop 24 may
also have means not shown for cooling and/or heating
20   the catholyte prior to its entry into chambers 20.

          It also has been found that the rate of
decomposition of the persulfate values may be decreased
without significantly affecting the cleaning power of
the regenerated solution by making a halide addition
25   to the anolyte. The halide addition has also been
found to increase overall cell efficiency. Generally,
about 10 ppm to about 500 ppm of a suitable halide
such as a chloride or a fluoride is added to the
anolyte. If a chloride is being added, the addition
30   should preferably be in the range of about 100 ppm to
about 200 ppm. If a fluoride is being added, the
addition should preferably be in the range of about
50 ppm to about 100 ppm. While the addition may be
made using any form of the halide, it is preferred to

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make an acid addition such as hydrochloric acid or hydrofluoric acid.

In operation, a voltage sufficient to cause a current density in the range of about 0.4 A/cm^2 to
5   about 1.0 A/cm^2, preferably from about 0.6 A/cm^2 to about 0.8 A/cm^2, is applied to the cell. A voltage in the range of about 4 to about 6 volts is generally sufficient to produce the desired current densities. Upon application of the voltage, the copper ions are
10   taken out of solution and plated onto the cathodes 50 while sulfate ions are oxidized to persulfate ions at the anode. There also tends to be some production of hydrogen gas at the cathode and oxygen gas at the anode; however, the production of these gases does not
15   hamper the regeneration process. In fact, they create a bubble lifting effect that promotes both anolyte and catholyte movement.

After the cleaning solution has been regenerated, it may be returned to the cleaning tank 10 through the
20   flow line 40. A valve 42 is provided in flow line 40 to permit recirculation of the solution to the anode chamber 12 via the flow line 44 if desired or if needed. To facilitate circulation of the cleaning solution, a pump 46 may be incorporated into the flow
25   line 40. If desired, a storage tank not shown for holding the regenerated cleaning solution until it is needed may also be incorporated into the flow line 40.

If adjustments in raw material concentration, solution temperature or other parameters are needed
30   prior to solution regeneration, the spent solution may be transferred from the cleaning tank 10 to a reconditioning unit 38. To do this, the spent solution is withdrawn from the tank 10 via line 17 and valve 36 in lieu of line 16 and valve 18. The reconditioning
35   unit 38 may comprise any suitable solution

reconditioning means known in the art. Of course, the type of reconditioning unit utilized will depend upon the type of adjustment that needs to be made to the spent solution. For example, reconditioning unit

5 38 may comprise means for cooling the spent solution or means for adding one or more raw materials to the spent solution. After the spent solution has been reconditioned, it may be transferred to the chamber 12 via the flow line 16.

10   The following examples are presented to demonstrate the present invention.

EXAMPLE I

To measure their cleaning power or etching rate, the following cleaning solutions were prepared: (1) an

15 aqueous peroxydisulfuric acid solution (PDA) containing 1.85M peroxydisulfuric acid and 200 ppm Cl^- maintained at 25°C; (2) a 12% H_2SO_4-3% H_2O_2-distilled water solution maintained at 43°C; (3) a 12% H_2SO_4-3% H_2O_2- tap water solution maintained at 43°C; (4) an aqueous

20 2N. ferric sulfate solution maintained at 80°C; and (5) an aqueous 2N. ferric sulfate solution containing 0.3M Cu^{2+} maintained at 80°C. The chloride addition to the peroxydisulfuric acid solution was made using HCl. 1" x 2" coupons of copper alloy C11000 were prepared

25 and weighed. Several coupons were then immersed in each solution for 15 seconds. After being removed, the coupons were rinsed in water and reweighed. The procedure was then repeated again with each coupon being reweighed a second time. The etching rate of

30 each solution is reported in Table I.

35

Table I

Solution	Etching Rate (mg/cm²/sec)
1.85M peroxydisulfuric acid w/200 ppm Cl⁻	.081
12% H_2SO_4-3% H_2O_2-distilled H_2O	.070
12% H_2SO_4-3% H_2O_2-tap H_2O	.011
2N. ferric sulfate	.120
2N. ferric sulfate + 0.3M Cu^{2+}	.095

EXAMPLE II

A 1.6M peroxydisulfuric acid solution $H_2S_2O_8$ was prepared and permitted to decompose at room temperature (22°C) to peroxymonosulfuric acid H_2SO_5. At various intervals, the solution was tested to measure its composition, in particular, the concentration of peroxydisulfuric acid and peroxymonosulfuric acid. During these intervals, coupons of alloy C11000 were immersed in the solution as in Example I. Prior to the first immersion and after each immersion, the coupons were weighed so that the solution's etching rate could be determined. As can be seen from Figure 3, the etching rate increased as the $H_2S_2O_8$ decomposed into H_2SO_5 until a point after the solution had a concentration of about 1.2M H_2SO_5 and about 0.4M $H_2S_2O_8$. Thereafter, the etching rate was slightly decreased. Figure 3 also illustrates the etching rate of the 1.6M peroxydisulfuric acid as it decomposes compared to the etching rate of other cleaning solutions.

EXAMPLE III

1" x 2" coupons of copper alloys C68800 and C65400 were prepared. The C68800 coupons were prepared from C68800 strip that had been bell annealed. The C65400 coupons were prepared from C65400 strip material that had been strip annealed.

The C68800 samples were first immersed in a
boiling caustic solution containing 1N NaOH. The
solution was at about 100°C. Different coupon samples
were immersed for different time intervals. The time
5 intervals were 10 seconds, 20 seconds and 30 seconds.
After being rinsed, some of the samples were immersed
in an aqueous 12% H_2SO_4-3% H_2O_2 solution which was at
about 43°C. The remainder of the coupons were immersed
in an aqueous peroxydisulfuric acid solution containing
10 1.8M peroxydisulfuric acid and about 200 ppm Cl^- which
was at about 25°C. The chloride addition to the
peroxydisulfuric acid solution was made using HCl.
The immersion time of the respective samples in each
cleaning solution reflected its immersion time in the
15 boiling caustic solution. For example, if the sample
had been immersed in the caustic solution for
10 seconds, it was immersed in the acid cleaning
solution for 10 seconds.

The C65400 samples were divided into two groups.
20 The first group was immersed in an aqueous 12% H_2SO_4-
3% H_2O_2 solution at about 43°C for the following time
intervals: 20 seconds; 30 seconds; and 40 seconds.
The second group was immersed in an aqueous
peroxydisulfuric acid solution containing 1.8M
25 peroxydisulfuric acid and about 100 ppm F^- at about
25°C. The fluoride addition was made as HF. The
C65400 samples were immersed in the peroxydisulfuric
acid solution for the following time intervals:
15 seconds; 25 seconds; and 35 seconds. None of the
30 C65400 samples were subjected to a caustic solution
pretreatment.

All of the samples were rinsed in water and dried
after immersion in the acid cleaning solution. The
samples were then evaluated by dip soldering in a
35 60% Sn-40% Pb solder bath at about 238°C. A resin

flux was applied prior to the dip tests. All samples
were immersed in the bath for five seconds and then
slowly pulled out. The solderability of the dipped
samples was subjectively rated using the following
5 system:

Class	Description
1	Uniform smooth coating
2	Uniform rough coating
2a	<5% dewetting
3	<50% dewetting <10% pinholes
4	>50% dewetting >10% pinholes
5	No adhesion

As can be seen from Table II, the samples of
C68800 and C65400 cleaned with the peroxydisulfuric
acid solution exhibited better solderability ratings -
the lower the class, the better the rating. With
20 respect to the C65400 samples, those cleaned in the
peroxydisulfuric acid solution exhibited better
solderability ratings with shorter immersion times.

Table II

Alloy	Treatment	Immersion Time (sec)	Solderability Rating
C68800	$NaOH/H_2SO_4-H_2O_2$	10	4
C68800	$NaOH/H_2SO_4-H_2O_2$	20	3-4
C68800	$NaOH/H_2SO_4-H_2O_2$	30	3-4
C68800	$NaOH/H_2S_2O_8$ w/200 ppm Cl^-	10	2
C68800	$NaOH/H_2S_2O_8$ w/200 ppm Cl^-	20	2
C68800	$NaOH/H_2S_2O_8$ w/200 ppm Cl^-	30	2

Table II (Cont.)

	Alloy	Treatment	Immersion Time (sec)	Solderability Rating
5	C65400	$H_2SO_4-H_2O_2$	20	4-5
	C65400	$H_2SO_4-H_2O_2$	30	3-4
	C65400	$H_2SO_4-H_2O_2$	40	2a
	C65400	$H_2S_2O_8$ w/100 ppm F^-	15	3
	C65400	$H_2S_2O_8$ w/100 ppm F^-	25	2
10	C65400	$H_2S_2O_8$ w/100 ppm F^-	35	2

EXAMPLE IV

To demonstrate the effect of temperature on the
stability of peroxydisulfuric acid solutions, solutions
initially containing 1.5M $H_2S_2O_8$ and about 2.5M $H_2S_2O_8$ were
15 prepared. None of these solutions contained a halide
addition. A portion of the 2.5M $H_2S_2O_8$ solution was
kept at 0°C and allowed to decompose for several days.
The 1.5M $H_2S_2O_8$ solution and the remainder of the
2.5M $H_2S_2O_8$ solution were kept at room temperature
20 (about 22°C) and allowed to decompose for several
days.

As can be seen from Figure 4, the solution at 0°C
retained a substantially constant total molarity. As
used herein, the total molarity is the sum of the
25 peroxydisulfuric acid molarity and the peroxymono-
sulfuric acid molarity. In comparison, the total
molarity of the solutions at room temperature
deteriorated rather rapidly.

EXAMPLE V

30 To illustrate the effect of a halide addition on
decreasing the decomposition rate of peroxydisulfuric
acid, an aqueous 1.6M $H_2S_2O_8$ solution was prepared.
100 ppm of F^- was added to the solution using
hydrofluoric acid. The solution with the halide

35

addition was kept at room temperature and permitted to decompose.

As can be seen from Figure 5, the amount of $H_2S_2O_8$ in the solution decreased rather rapidly while

5 the amount of H_2SO_5 in the solution increased. As a result, the total molarity, the sum of $H_2S_2O_8$ and H_2SO_5 in solution, remained substantially constant. It can be seen from Figure 5 that when the concentration of H_2SO_5 starts to decrease, the

10 concentration of H_2O_2 increases. This clearly demonstrates the decomposition mechanism of peroxy-acids discussed hereinbefore.

By comparing the total molarity curve of Figure 5 with the total molarity curve of the 1.5M

15 solution in Figure 4, it can be seen that the addition of a halide to the peroxydisulfuric acid solution decreases its rate of decomposition as represented by total molarity.

EXAMPLE VI

20 To illustrate the effect of a halide ion addition on the generation of peroxydisulfuric acid in an electrochemical cell such as the one shown in Figure 2, several aqueous 20 v/o H_2SO_4 solutions were prepared. The following additions were made to various samples of

25 the H_2SO_4 solution: (a) 100 ppm Cl^-; (b) 200 ppm Cl^-; and (c) 100 ppm F^-. The chloride additions were made as hydrochloric acid and the fluoride addition was made as hydrofluoric acid.

The solutions with the halide additions were used

30 as the anolyte in the cell. For comparison purposes, an aqueous 20 v/o H_2SO_4 solution without any halide addition was also used as an anolyte in the cell. For all tests, the catholyte was an aqueous 20 v/o H_2SO_4 solution. The anode and cathode chambers of the cell

35 were separated by a Nafion membrane and an aqueous

glycol solution at about 0°C was circulated through
the anode chamber during each test. During the
peroxydisulfuric acid generation process, the anolyte
was maintained at a temperature in the range of 5°C

5 to 8°C. A current density of 0.4 A/cm² at a voltage
of 5.5V was applied to the cell.

As can be seen from Table III, the halide addition
to the anolyte tended to improve cell efficiency. As
used herein, cell efficiency may be defined as the

10 amount of charge theoretically needed to convert 100%
of the sulfuric acid to $H_2S_2O_8$ divided by the actual
charge used to generate the peroxydisulfuric acid.

Table III

Halide Addition (ppm)	Peroxydisulfuric Acid (molarity)	Cell Efficiency (%)
None	1.6	11
100 Cl^-	1.6	22
200 Cl^-	1.8	37
100 F^-	1.8	40

15

20   EXAMPLE VII

To demonstrate the effect of temperature on cell
efficiency and $H_2S_2O_8$ generation, an aqueous
20 v/o H_2SO_4 solution containing 100 ppm F^- was
prepared as in Example VI and introduced into the cell

25 of Figure 2 as the anolyte. As before, an aqueous
20 v/o H_2SO_4 solution without any halide was used as
the catholyte, Nafion membrane separated the anode and
cathode chambers, and an aqueous glycol solution was
circulated through the anode chamber. A current

30 density of 0.6 A/cm² was applied across the cell.

As can be seen from Figure 6, cell efficiency
decreased as anolyte temperature increased.

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Furthermore, the rate of peroxydisulfuric acid production tended to be higher for the lower temperatures.

EXAMPLE VIII

5   To demonstrate the effect of current density on cell efficiency and peroxydisulfuric acid generation, an aqueous sulfuric acid solution containing 100 ppm F^- was prepared as in Example VI and introduced into the cell of Figure 2 as the anolyte. The other cell

10   conditions were the same as in Example VII except that the anolyte temperature was maintained at 11°C and a current density of 0.4 A/cm^2 was applied during one test and a current density of 0.6 A/cm^2 was applied during a second test. It can be seen from Figure 7

15   that the higher the current density, the better the cell efficiency and the rate of production of peroxydisulfuric acid.

While a particular type of electrochemical cell has been illustrated to regenerate the peroxydisulfuric acid cleaning solution, other types of electrochemical

20   cells could be utilized.

While any suitable heat exchange fluid at any desired temperature may be circulated through the anode chamber to control the temperature of the anolyte as needed, it is preferred to use an aqueous glycol

25   solution at a temperature of about -5°C to about 5°C, most preferably at about 0°C, as the heat exchange fluid.

While the examples illustrate the use of peroxydisulfuric acid solutions to clean copper alloys

30   C11000, C65400 and C68800, the solution may be used to clean copper and other copper alloys. Depending upon the type of copper or copper base alloy forming the material to be cleaned and the nature of the contaminants on the material, it may be desirable to

35   pretreat the material prior to its immersion in the

peroxydisulfuric acid solution. Any suitable
pretreatment such as immersion in a boiling caustic
solution or mechanical action may be used.

    Preferably, the peroxydisulfuric acid cleaning
5 solution of the present invention is a non-chromium
containing solution that does not initially contain
any significant amount of any other mineral acid.

<u>CLAIMS</u>

1.   A process for the cleaning or etching of copper and copper base alloys which comrises contacting the copper or copper base alloy with an aqueous oxidising acid solution, characterised in that the aqueous oxidising acid solution used is a chromium free 1N to 5N aqueous solution of peroxydisulfuric acid.

2.   A process according to claim 1, characterised in that said peroxydisulfuric acid solution has a concentration of from 1.5N to 2.5N.

3.   A process according to claim 1 or 2, characterised in that the copper or copper base alloy is contacted with said aqueous peroxydisulfuric acid solution at a temperature in the range 15-30°C.

4.   A process according to claim 3, wherein said temperature is in the range 20-25°C.

5.   A process according to any one of claims 1-4 characterised in that the spent etching solution is electrolytically regenerated and dissolved copper recovered by feeding the spent solution as an anolyte to the anode compartment of a compartmental electrolyte cell containing 10-50% by volume aqueous sulfuric acid as the catholyte in the cathode compartment, applying an electric current to said cell, and recovering from the cell cathodically deposited copper from the cathode compartment and regenerated etching solution from the anode compartment.

6.   A process according to claim 5, characterised in that from 10 to 50 ppm of a water soluble halide are added to the spent electrolyte in the anode compartment of said cell.

7.   A process according to claim 6, wherein said halide is hydrochloric acid added in an amount of 100 to 200 ppm, or hydrofluoric acid added in an amount of from 50 to 100 ppm.

8.   A process according to claim 5, 6 or 7, characterised in that the temperature of the anolyte during the regeneration step is maintained in the range 0-20°C and the electric current is applied at a current density in the range 0.4 to 1 A/cm^2.

9.   A process according to claim 8, wherein said temperature is in the range 0-10°C and said current density is in the range 0.6 to 0.8 A/cm^2.

10.   A process according to claim 8 or 9, wherein the temperature of the anolyte is controlled by circulating a fluid cooling medium through the anode.

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Fig-1

Fig-2

Fig-3

Fig-4

0138531

Fig-5

Fig-6

Fig-7

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
D,Y	US - A - 3 671 344 (J.S.C. CHIANG et al.) * Column 3, lines 43-55, claims *	1,3	C 23 G 1/10 C 23 G 1/36 C 23 F 1/18 C 25 F 7/02
Y	EP - A1 - 0 082 210 (MTA MÜSZAKI FIZIKAI KUTATO INTEZETE) * Claims 1,2 *	1	
D,X	US - A - 3 470 044 (K.J. RADIMER) * Fig.; claims *	5	
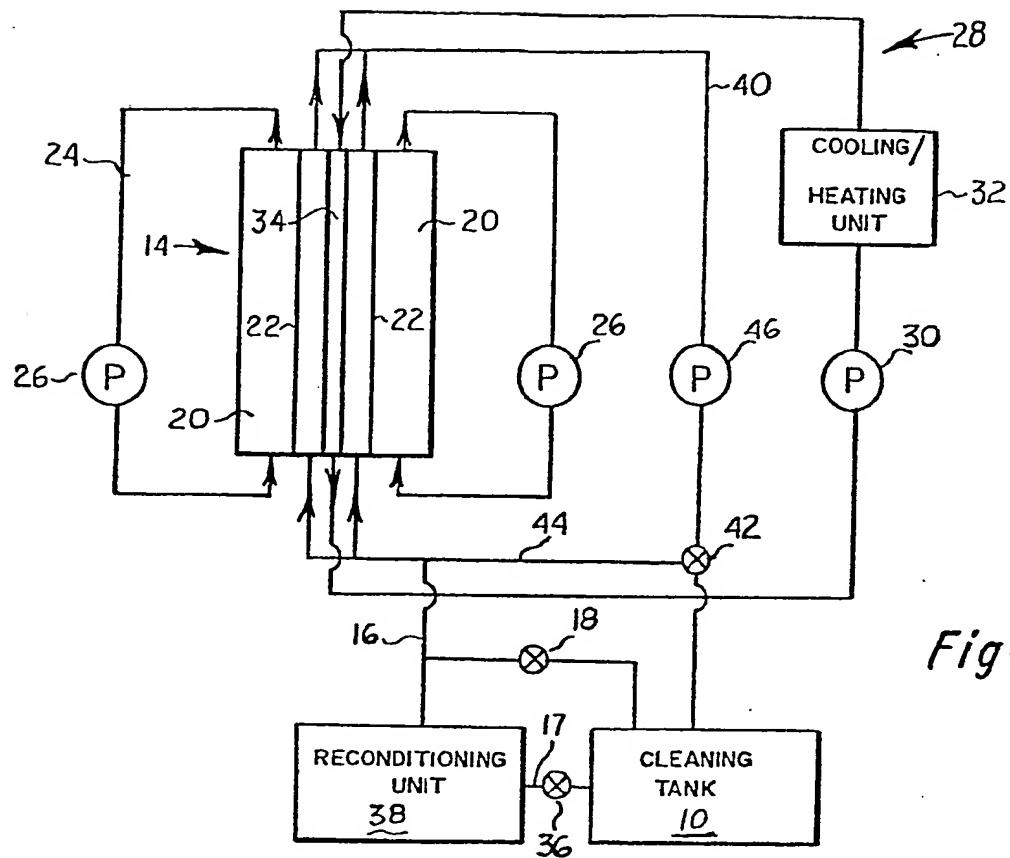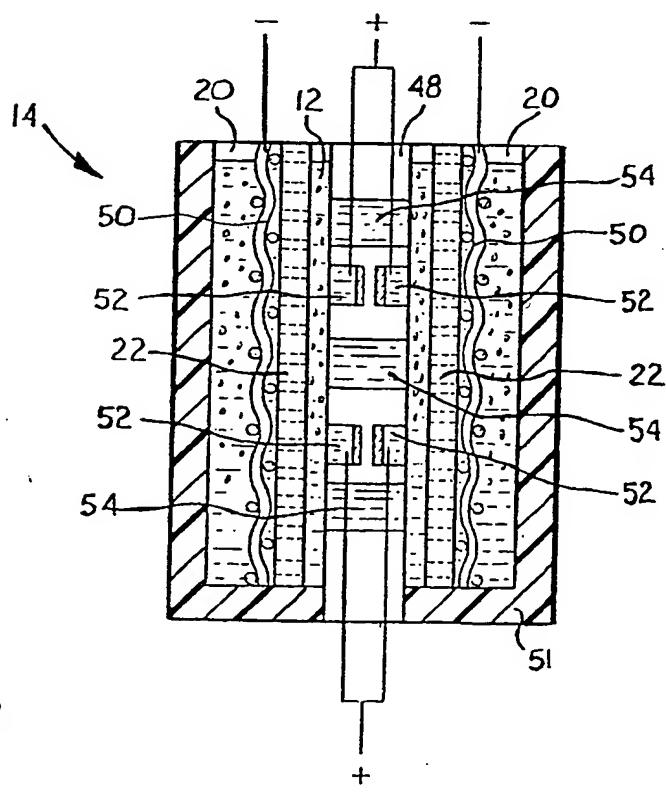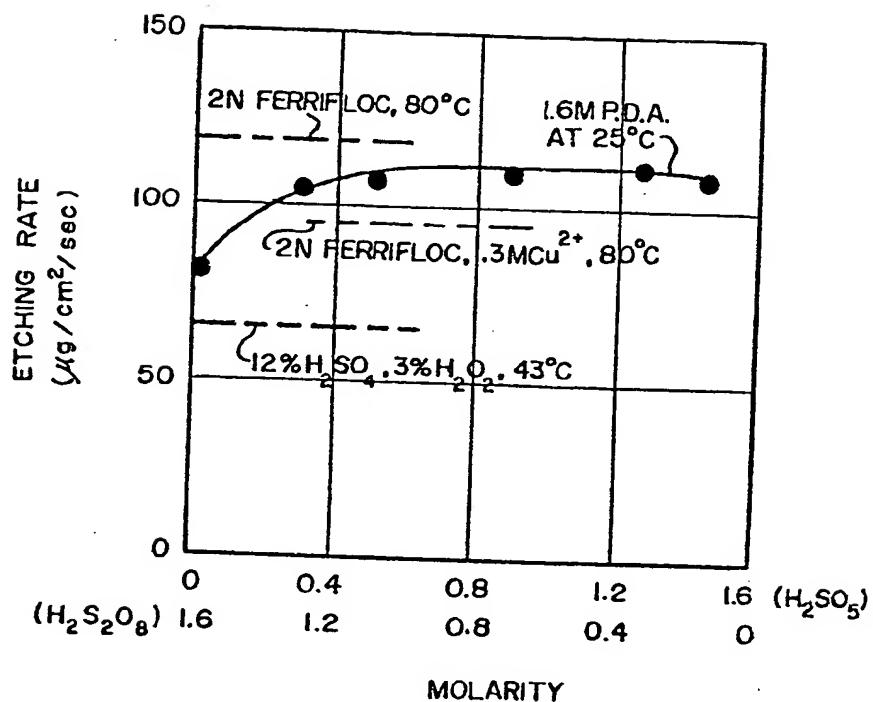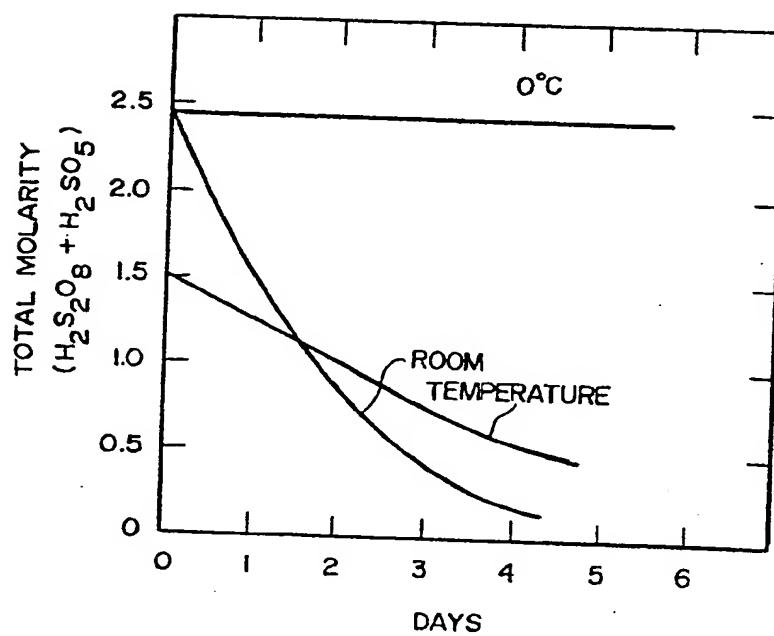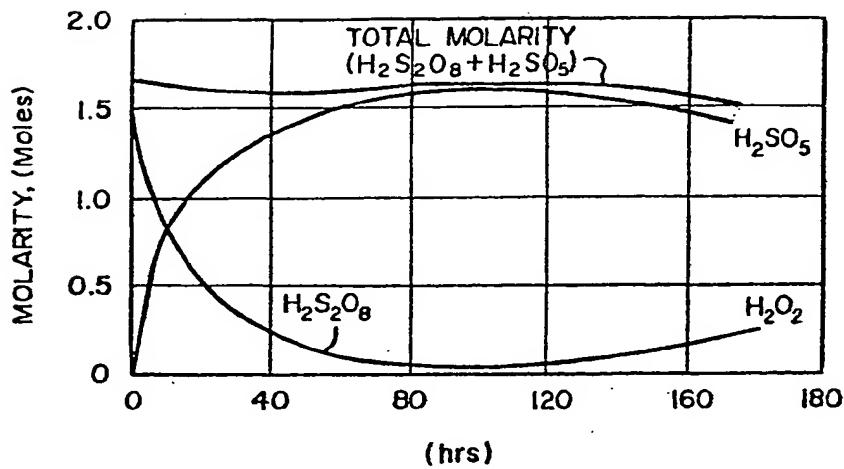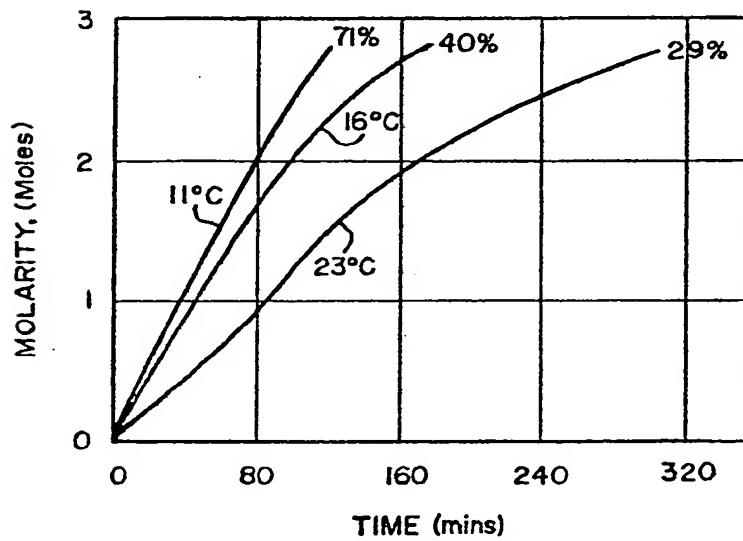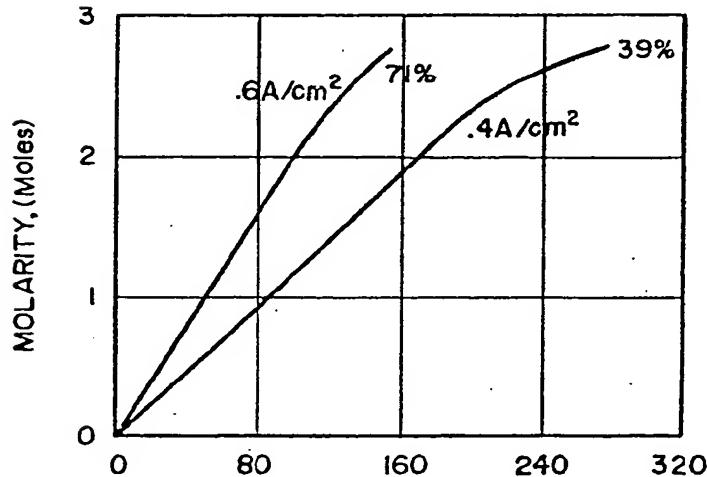
DOCUMENTS CONSIDERED TO BE RELEVANT EP 84306812.3

TECHNICAL FIELDS
SEARCHED (Int. Cl.4)

C 23 G
C 23 F
C 25 F

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
VIENNA	12-12-1984	SLAMA